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RESEARCH ARTICLE

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Key Points:

- Models C turnover for diurnal cycles
- Model included both DOC and POC
- Correctly modeled 60% to 70% loss in 2 days

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Modeling the rate of turnover of DOC and particulate organic carbon in a UK, peat-hosted stream: Including diurnal cycling in short-residence time systems

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Abstract This study proposes a multicomponent, multiprocess scheme to explain the turnover of organic matter (particulate and dissolved organic matter) in streams. The scheme allows for production and degradation of organic matter by both photic and aphotic processes with transformation of dissolved organic carbon (DOC) to increasingly refractory forms. The proposed scheme was compared to 10 months of experimental observations of the turnover and fate of particulate and dissolved organic matter in stream water from a peat-covered catchment. The scheme was able to explain average decline in DOC concentration of 65% over 70 h with a 13% mean average percentage error based on turnover in three types of organic matter (particulate, labile dissolved, and refractory dissolved) although the order and rate of reactions did change between sets of experimental observations. The modeling suggests that activation energies are low for all except the most refractory forms of DOC in turn, suggesting that processes are not sensitive to temperature change. Application of the modeling scheme to organic matter turnover in the River Tees, northern England, showed that annual removal of total organic carbon was equivalent to between 13 and 33 t C/km²/yr from an at source export of between 22 and 56 t C/km²/yr giving a total in-stream loss rate of between 53 and 62% over a median in-stream residence time of 35 h.

1. Introduction

Although the importance of the fluxes of dissolved organic carbon (DOC) and particulate organic carbon (POC) to terrestrial carbon budgets has been widely recognized [e.g., *Battin et al.*, 2009], the impact of these carbon fluxes on the presence of carbon greenhouse gases in the atmosphere can only be understood if the turnover of DOC and of POC is measured. The Inter-governmental Panel on Climate Change now include an estimate of global DOC flux [*Solomon et al.*, 2007] but do not yet consider any losses of DOC in stream, and so this flux value has no direct impact upon atmospheric greenhouse gases. Several attempts have been made to estimate the flux of carbon from the terrestrial biosphere [*Meybeck*, 1993]. *Ludwig et al.* [1996] estimates the global fluvial flux of DOC to be 200 Mt C/yr, with a POC flux of 100 Mt C/yr. *Worrall et al.* [2007] estimated the average annual fluvial DOC flux from the UK as 969 kt C yr⁻¹ and the average annual POC flux of 554 kt C yr⁻¹.

Cole et al. [2007] have estimated that at a global scale 1.9 Pg C/yr enters rivers of which 0.8 Pg C/yr (42% of the input) is returned to the atmosphere, while *Battin et al.* [2009] suggested a lower limit of 21% removal of DOC in stream. However, other studies have found higher values. For Sweden, *Jonsson et al.* [2007] estimated that around 50% of terrestrially derived organic carbon was mineralized for a lake catchment where residence times would be long relative to the UK, and *Humborg et al.* [2010] have estimated that for Sweden the loss from the terrestrial biosphere to the fluvial network (streams and lakes) was 4.57 Mt C/yr of which 56% was total organic carbon (TOC) and 47% of this TOC was lost (1.2 Mt C/yr) in the fluvial network, and 56% of the total carbon (inorganic and organic) inputs from the terrestrial biosphere were lost to the atmosphere in the fluvial network. *Striegl et al.* [2012] found a very similar proportion of total carbon lost to the atmosphere for the Yukon river basin, i.e., 50% of the total carbon flux of the river was lost to the atmosphere. *Worrall et al.* [2012] used empirical and structural modeling of the DOC export from over 194 catchments across the UK, across 7 years; and allowed for differences in the catchments soil, land use, and hydroclimatic characteristics; and found a net watershed loss of DOC up to 78% (equivalent to between 9.0 and 12.7 t C/km² of UK land area/yr). *Wallin et al.* [2013] considered a 67 km² boreal catchment

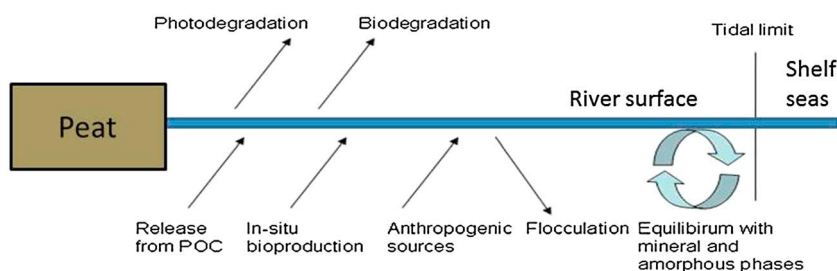


Figure 1. Schematic diagram of the DOC processing within a peat-sourced stream.

and found that CO_2 evasion from the streams represented 53% of the flux of carbon in the streams and showing that organic matter turnover was rapid in low-order streams. *Moody et al.* [2013] considered empirical studies of DOC turnover, and over a 10 day time scale, the median loss was 73% with 60% of loss occurring in the first 2 days. *Moody et al.* [2013] modeled their data on a daily basis, but the results suggest that given the scale of the losses after just 2 days then modeling on a subdaily basis would be advisable. Equally, *Worrall et al.* [2014] showed that for the relative unimpounded UK catchments tend to have in-stream residence time of less than 3 days with median values of in-stream residence time being between 1 and 2 days.

Particulate organic carbon can also turnover but there are fewer specific studies. The decline in sediment yield through a catchment has often been expressed as a sediment delivery ratio [e.g., *Walling*, 1983]. This decline in sediment yield has been associated with storage of suspended sediment in channel [e.g., *Collins and Walling*, 2007] and on floodplains [e.g., *Walling and Owens*, 2003]. Although studies have considered spiralling of organic matter [*Newbold et al.*, 1982], they have not considered loss by turnover [e.g., *Young and Huryn*, 1997; *Griffiths et al.*, 2009]. *Van Oost et al.* [2007] considered the transfer of eroded sediment through a catchment into burial and the sink of carbon represented by replacement in the soil source, and this gave an estimated global carbon sink due to soil erosion of 0.12 Pg C/yr but did not consider loss of particulate organic carbon in the streams of the catchment.

Therefore, this study considers the loss of POC and DOC in a peat-hosted stream over periods of days including diurnal cycles.

2. Approach and Methodology

Within streams, there are a range of processes that could remove, degrade, or add DOC (or POC) to the water (Figure 1). In this approach we assume that DOC released from soil into stream water can undergo both biodegradation and photodegradation that may transform DOC not only into CO_2 or CO but also into increasing recalcitrant forms of DOC. The stream water contains POC which can also be transformed into CO_2 ,

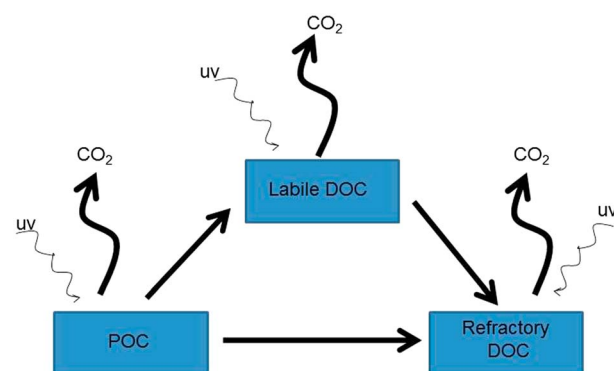


Figure 2. Schematic diagram of the scheme proposed in this study for three forms of organic matter—POC, labile DOC, and a refractory DOC component.

CO, or DOC. The difference between DOC and POC is commonly operationally defined by filter size, and this study uses a filter cutoff of 0.45 μm to distinguish and define POC and DOC. The schematic representation of the DOC transformation is given in Figure 2. In this scheme it is possible to envisage a range of distinct DOC forms that have distinct character, but the scheme assumes that POC degrades first to the most labile form of DOC and not immediately to the more recalcitrant forms. Each form of DOC and POC can have distinct rates of biodegradation and photodegradation and indeed production. This scheme assumes that the POC remains

in suspension and, based on experiments for the study river (C. S. Moody, Is peat erosion a source of CO₂?, Univ. of Durham, Durham, U. K., unpublished PhD thesis, 2014), that there is no significant adsorption or desorption of DOC to or from the POC. Equally, this scheme assumes no significant flocculation of DOC (based upon *Moody et al.* [2013]), but it does allow for in-stream production of DOC and POC. The scheme could include multiple and progressively more refractory, or indeed more labile, forms of DOC.

For a scheme where there are increasingly refractory forms of DOC, the total observable DOC concentration is given by

$$[\text{DOC}]_{\text{obs}} = \sum_{n=1}^n [\text{DOC}]_n \quad (1)$$

where $[\text{DOC}]_x$ = DOC concentration (mg C/L), where x is Obs = the observed DOC concentration, and n = the DOC concentration of DOC fraction n with 1 the most labile form to n the most recalcitrant form. The rate of change of each form of DOC then takes the form for $n = 1$ as

$$\frac{d[\text{DOC}]_1}{dt} = -k_1[\text{DOC}]_1^\beta + \frac{\alpha_1 \text{PAR}}{\alpha_1 \text{PAR} + K_{\text{Max}1}} [\text{DOC}]_1 + \mu_1 ([\text{POC}]_0 - [\text{POC}]) \quad (2)$$

And for $n > 1$,

$$\frac{d[\text{DOC}]_n}{dt} = -k_n[\text{DOC}]_n^\gamma - \frac{\alpha_n \text{PAR}}{\alpha_n \text{PAR} + K_{\text{Max}n}} [\text{DOC}]_n + \mu_n ([\text{DOC}]_0 - [\text{DOC}]_{n-1}) \quad (3)$$

where k_n = a rate constant for fraction n ((mg C/L)^{1-x}/h), where x is β , γ which are rate orders, α_n = the apparent quantum yield (AQY—mg C/L/h/W/m²), PAR = photosynthetically active radiation (W/m²), $K_{\text{Max}n}$ = the maximum rate of photodegradation for fraction n (mg C/L/h/W/m²), μ_n = the proportion of the previous fraction of DOC or of the POC that changes into the subsequent fraction, and $[\text{DOC}]_0$ = the initial concentration of DOC (mg C/L). It should be noted that in this model scheme there is no absolute reason for progressive DOC phases to be progressively more refractory, and no constraint was put on the rate constants.

The rate of change of the POC concentration is given by

$$\frac{d[\text{POC}]}{dt} = -k_{\text{POC}}[\text{POC}]^\delta + \frac{\alpha_{\text{POC}} \text{PAR}}{\alpha_{\text{POC}} \text{PAR} + K_{\text{MaxPOC}}} [\text{POC}] \quad (4)$$

where $[\text{POC}]$ = the particulate organic carbon concentration (mg C/L). Unlike equations (2) and (3), equation (4) has no addition from other phases because the scheme assumes that there is nothing that adds to the initial POC; however, no constraint was put on μ and so production of POC was possible. Further, the rate constants were allowed to change with temperature according to the van't Hoff equation and then both temperature and PAR were allowed to vary over time.

$$k_n = A_n e^{-E_{\text{act}}/RT} \quad (5)$$

$$\text{PAR} = f(t) \quad (6)$$

$$T = g(t) \quad (7)$$

where T = absolute temperature (K), t = time since start of experiment (h), A_n = constant, E_{act} = activation energy for rate constant k_n (kJ/g C), and R = universal gas constant (g C/kJ/K).

The system of equations was solved using a Runge-Kutta method with $\Delta t = 1$ h and fitted to observed data using maximum likelihood. The number of DOC fractions to be considered and the order of the reactions describe and delimit the number of parameters required to fit observed changes in DOC. Thus, the Akaike information criterion (AIC) was used to assess the appropriate number of fractions (n) and orders of reactions (β , δ).

2.1. Degradation Experiments

In situ degradation measurements of DOC were conducted for a headwater river in a peat-covered catchment. A first-order stream in a peat-covered catchments was chosen as it could be expected to be closest to soil water source of DOC and POC, i.e., the samples were the freshest possible.

The primary site was the headwaters of the River Tees (Cottage Hill Sike and Trout Beck—Figure 3). The River Tees flows 132 km from its source in the Moor House National Nature Reserve, before draining in to

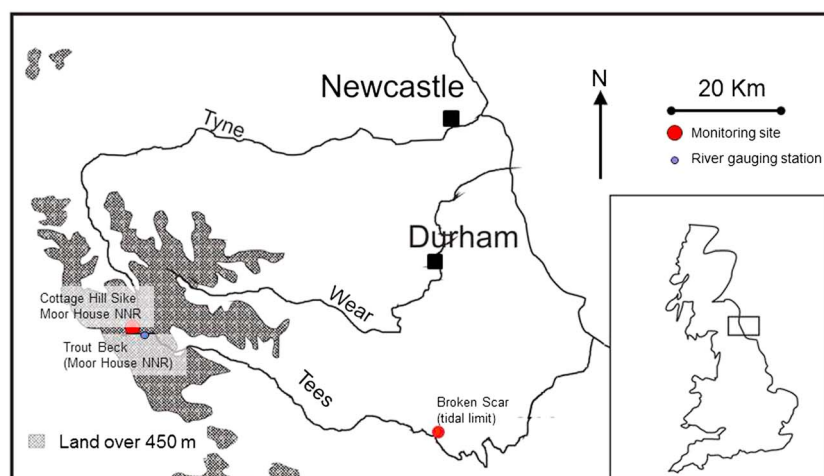


Figure 3. Location of the study catchment with the sampling point S (Cottage Hill Sike and Trout Beck) within the Moor House National Nature Reserve (MH NNR), tidal limit (Broken Scar), and river flow-gauging stations used within the study.

the North Sea, although the estuary is cut off by a total exclusion tidal barrage. The sampling site was on the Cottage Hill Sike within the Moor House National Nature Reserve (MH NNR), the most extensively studied of all UK peatlands [Billett *et al.*, 2010].

The degradation measurements were made outside of the laboratory in ambient light and temperature conditions (rather than indoors under artificially controlled conditions). The study considered degradation in light over time scales relevant to river residence times (i.e., 70 h, approximately 3 days). Experiments were conducted each month for 10 months from December 2011 to November 2012 with samples not available for January 2012 due to frozen conditions restricting access to the field site and running stream water. The distribution of sampling across the year was chosen so as to experience a range of both meteorological conditions and of DOC (POC) concentrations and compositions. The samples were not prefiltered so as not to exclude particulates, rather particulates were left in the samples. Including the particulates within the study samples meant that the study considered the net fate of DOC and could include production from POC—it is common to study only DOC, e.g., Kohler *et al.* [2002] did remove particulates from their incubations.

Degradation experiments for the Cottage Hill Sike spanned up to 70 h with sacrificial sampling taking place at 0, 1, 2, 4, 9, 22, 30, 48, 56, and 70 h since the start of the experiment. On each day of sampling the experiments started at noon. Replicates were included for each sample except for time zero samples. The sampled water was then poured into acid-washed, quartz glass tubes, stoppered with a rubber bung at the bottom, and loosely stoppered at the top. Quartz glass allows all light wavelengths to pass through it. The quartz glass tubes had a diameter 55 mm and filled to give a water depth of approximately 150 mm. An examination of the flow stage records for the sample stream showed that 150 mm was the 46.5th percentile flow depth, i.e., 150 mm represented almost median flow depth in the source stream. Light attenuation can be considerable in colored waters, and Buckaveckas and Robbins-Forbes [2000] have related light attenuation to DOC in 74 Adirondack lakes. Taking the best fit equation from Buckaveckas and Robbins-Forbes [2000], the half depth of light attenuation could be calculated for the study catchment at the source water in the Cottage Hill Sike and for the measured DOC concentrations (1993–2010—see below for further details) the interquartile range of half depth of light attenuation was 150 to 340 mm, i.e., the quartz tubes selected represented 100% of the light penetration 25% of time but 62.5% of the light penetration 75% of the time. Furthermore, at the tidal limit of the study catchment (only a median water transit time of 35 h from Cottage Hill Sike [Worrall *et al.*, 2014]), the half depth of light attenuation has an interquartile range of 62 to 102 mm, but examining the flow stage duration for the tidal limit shows that even 62 mm water depth was only exceeded on 17% of days and 102 mm was exceeded on only 7% of days, i.e., there was almost full light penetration most of the time. Of course, such a light penetration calculation estimates the light conditions experienced by the base of the quartz tube while DOC molecules will move up and down the water column in the quartz tube on convective currents and so experience a range of light conditions greater than those estimated above.

All samples were left outside in trays, with all tubes lying at an angle to prevent rainfall entering and the sample evaporating or pouring out. The positioning of the tubes also stopped the light samples being shaded by the top bung and exposed a larger surface area of water to light. The samples were moved to different positions daily to avoid any bias in shading. Photosynthetically active radiation (PAR) and air temperature were logged hourly throughout all experiments. The vials were not continuously stirred but were agitated daily, and so it would be expected that suspended would not stay in suspension.

Because of the time related to the process of sample analysis, 2 mL of each sample from each quartz tube was treated at the time of sampling with 0.5 mL of concentrated sulphuric acid to fix the sample and prevent further degradation. Concentrated sulphuric acid was used because it is the first step in the analysis of DOC concentration using the method of *Bartlett and Ross* [1988]. Once fixed with concentrated sulphuric acid, the DOC concentration of the sample could be completed at a later time. This approach was used so that the degradation of the freshest samples could be considered from as near as possible to point at which they entered stream water from the peat profile.

Suspended sediment concentration was measured in samples from each monthly experiment and was measured in samples at 0, 30, and 70 h, resulting in 52 measurements across all the months of degradation experiments including duplicates. Samples were filtered through preweighed, 0.45 μm glass fiber filters, dried to 105°C, and the filter paper reweighed to give the concentration of particulate matter. The composition of the particulate matter was not analyzed, and particulate concentrations were only measured in a sample of 50 mL volume.

2.2. Application

The application of the preferred scheme derived from the fit of experiments will require parameter estimates for constants in equations (1) through (5): the time series of the temperature and PAR (i.e., equations (6) and (7)); an estimate of the time over which the turnover processes will operate; and the time series of the initial POC and DOC concentrations, i.e.,

$$[\text{POC}]_0 = h(t) \quad (8)$$

$$[\text{DOC}]_0 = i(t) \quad (9)$$

Parameter estimates for: k_n , β , γ , α_n , $K_{\text{max}n}$, μ_n , A_n , and E_{act} , will be taken from the best fit of the equations (1)–(5) to the experimental data.

The Cottage Hill Sike is part of the Environmental Change Network (ECN) monitoring program which means that hourly meteorological records for the site exist from 1993 onward. The meteorological records include air temperature and solar radiation from which input time series of stream temperature and PAR can be derived. For the application of the model, we will assume that air temperature is a reasonable estimate of the stream temperature except that we will assume the stream water does not freeze, for air temperature $< 0^\circ\text{C}$, $T = 0.1^\circ\text{C}$. Solar radiation can be readily related to PAR given the following equations derived for the site [Worrall *et al.*, 2009], for solar radiation > 0 then

$$\text{PAR} = 19.39 + 1.79S \quad (10)$$

where S = solar radiation (W/m^2). For $S = 0$, $\text{PAR} = 0$.

Also, as part of ECN monitoring within the Moor House NNR, the DOC concentration of the Cottage Hill Sike has been measured since 1992 although complete calendar years of weekly samples measured for DOC concentrations were only available from January 1993 [Worrall *et al.*, 2009]. Weekly concentration measurements of stream water DOC were not sufficient for modeling on a subdaily time step, and so weekly concentration data were placed in context and the best fit linear equation derived. The weekly DOC concentration were placed into context by comparing with the hourly meteorological records for the site and hourly discharge records for the Trout Beck stream (Figure 3). There are no flow records for the Cottage Hill Sike itself but from 1992 hourly stream discharge records are available for the Trout Beck stream: for the process of this model application it was assumed that the DOC concentrations are true for the flows recorded at the Trout Beck stream gauge. This means that concentrations of DOC measured in weekly samples could be compared to the instantaneous flow, the air temperature, PAR, month of the year, and the flows for each of the 24 h prior to the measurement. The month number (m , where January = 1 to

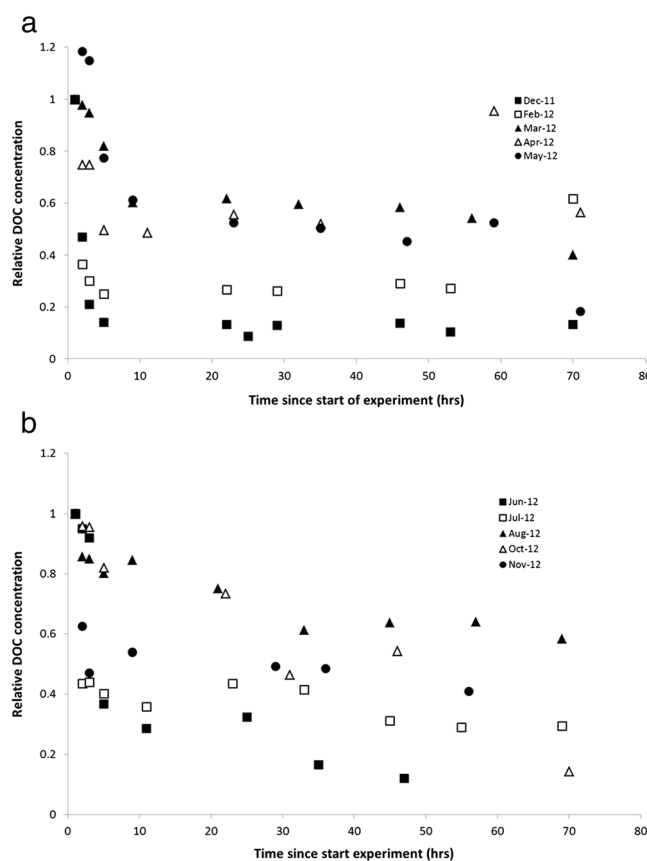


Figure 4. The average, relative DOC concentration change over the period allowed in the study. (a) December 2011 to May 2012 and (b) June 2012 to November 2012. Error bar is given as the standard error but smaller than symbol size used.

from the source to the tidal limit, or some other point of interest downstream. For the study in this catchment, the travel time was calculated from knowledge of the flow rates through the catchment. The travel time over which turnover occurred was calculated for each hourly discharge measured at the Trout Beck gauging station using the method of Worrall *et al.* [2014]. The method of Worrall *et al.* [2014] solves the Manning Equation for flow velocity [Manning, 1891] for the length of the river, from the source to a monitoring point of interest, given a formula for the change in cross-sectional area, wetted perimeter, and bed slope along the length of the river. This method has already been calibrated and tested for the River Tees of which the Cottage Hill Sike and the Trout Beck are tributaries.

The above approach to applying the best fit kinetic scheme does include a range of uncertainties. First, it was assumed that there was no substantial error or uncertainty in flow and meteorological data used. Second, the 10 sets of monthly degradation experiments provided 10 sets of consistent input parameters. However, it was not considered possible to assess which input parameter data set was most appropriate for which conditions were occurring during each and every hour of the period being modeled. So for each hour time step one of the 10 fitted input parameter data sets was chosen at random and applied for that hour. Third, the equations used to derive the time series of $[POC]_0$ and $[DOC]_0$ had an associated residual error after calculation of the best fit equation, i.e.,

$$[POC]_0 = h(t) + e_1 \quad (12)$$

$$[DOC]_0 = i(t) + e_2 \quad (13)$$

where e_x = the residual error. The distribution of the residual error was estimated from the fit of equations (12) and (13) to the observed data for Moor House and then the 100 time series of $[DOC]_0$ and $[POC]_0$ were generated from which the median, 25th and 75th percentile series were calculated. The 10 sets of kinetic

December = 12) was transformed as $\sin(m\pi/6)$ and $\cos(m\pi/6)$, and all other variables were considered both untransformed and log-transformed. Regression was performed in a stepwise manner with the significance of a variable being different from zero at the 95% probability being the threshold for inclusion.

Unfortunately, POC was not measured routinely in the stream water of the study catchment; however, Worrall *et al.* [2009] were able to estimate POC flux for the catchment based upon a rating curve for suspended sediment for the catchment:

$$[POC]_t = \phi(5.38 \ln Q + 17.16) \quad (11)$$

where ϕ = the fraction of the suspended sediment that was organic carbon and Q = the stream discharge at time t (m^3/s). This equation was applied given the hourly flow records from the stream gauge on the Trout Beck stream and given the assumption that the suspended sediment was 100% organic matter in this catchment and that the organic matter was 50% carbon.

The time over which turnover processes were assumed to operate is the time it takes for the river to flow

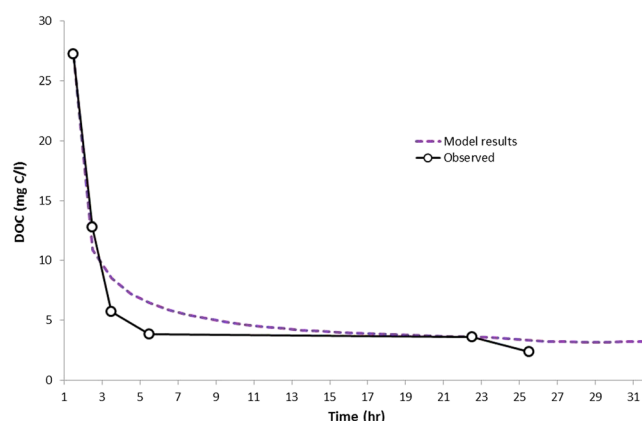


Figure 5. Fit of the model to the data from December. Error bar in the experimental observations is given as the standard error but smaller than symbol size.

and in most cases in the first 10 h (Figures 4a and 4b). In several cases there were periods when the DOC concentration increases between samplings most of these occur after the first day of the experiment but in one case DOC production was observed over the first 4 h of the experiment (12 May 12—Figure 4a). The average decline in POC concentration over 70 h across all months was 24%. The average final POC concentration was 30 mg C/L, with a standard error of 8 mg C/L. In four out of the 10 sets of monthly experiments the POC concentration did increase between the beginning and end of the experiment.

The fit of the model as assessed by AIC shows that for all 10 months of data the best fits were achieved for one type of POC and two of DOC. The use of AIC suggested that the order of the POC turnover and that of the second DOC component was always 1 (equation (4), $\delta = 1$ and equation (3) $\gamma = 1$). However, the AIC indicated that the order of the first DOC component (equation (2), β) varied between $n = 1$ to 3, although 2 was the most common. The root-mean-square error of the model with one POC and two DOC components varied from 1 to 27% with the average being 13% over all 10 experiments. The model fits particularly well over the first 24 h of each experiment, and this was when the majority of DOC loss occurred (Figure 5). The experimental data do show that over some periods of time there is a net increase in DOC, and the proposed rate equations were capable of representing this (Figure 6). Times of net DOC production occurred twice in the first 4 h, but the most common period of net DOC production was during the second half of the first day, i. e., during the first night of the experiment. Given the proposed rate equations, there is a ready explanation for this observation. The POC turns over to produce DOC during daylight hours which itself is readily turned over, but during nighttime the produced DOC is not quickly turned over and the aphotic turnover of POC to produce DOC is faster than the aphotic turnover of that DOC, and thus, DOC concentration increases during the hours of darkness. However, the buildup of DOC is of the labile DOC which is readily turned over after daybreak when photic degradation can start again.

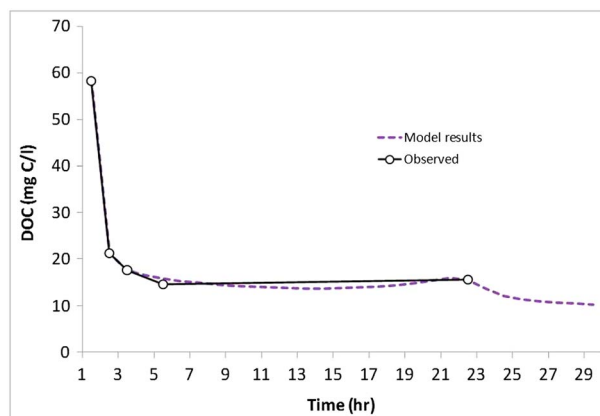


Figure 6. The fit of the model scheme for the data collected in February 2012 showing an example of an observed overnight increase in DOC concentration predicted by the model scheme. Error bar is given as the standard error but smaller than symbol size.

parameters derived from the fit of equations (1) through (5) to the experimental observations and three sets of time series were applied to hourly data for Cottage Hill Sike for the 3 years 1996, 1997, and 1998. These 3 years were chosen because they are the first years in the record for the catchment which were complete and did not include the drought year of 1995.

3. Results

The average decline in DOC concentration over 70 h across all months of sampling was 65% but with 59% loss occurring over the first 30 h

The best fit models for each of the 10 sets of experiments can be interpreted in terms of mechanism. For the POC the parameters describing the aphotic degradation (Table 1) fall into three patterns. Between December and April values of E_{act} are so small that it is in effect zero, and so there is negligible change in

Table 1. The Summary of Model Parameters for the Turnover of POC

Month	[DOC] ₀	[POC] ₀	A	E _{act}	K _{max1}	α	Fraction (μ)
Dec	27	10	0.010	0.00000	1.000	−0.00011	0.95
Feb	58	26	0.010	0.00000	1.000	0.00056	0.95
Mar	30	10	0.000	0.00000	1.000	−0.00002	0.95
April	57	25	0.081	−0.01686	1.002	−0.00170	0.61
May	28	24	−0.081	−0.01686	1.000	0.00420	0.85
June	33	23	0.123	−0.05387	1.008	−0.00092	0.33
July	50	14	0.193	−0.07612	1.004	−0.00302	0.12
Aug	47	105	0.123	−0.05384	1.008	−0.00328	0
Oct	33	38	0.117	−0.05029	1.008	−0.02815	0.02
Nov	57	26	0.122	−0.05335	1.008	−0.01229	0.05

rate of turnover with temperature. During these experiments the aphotic rate of turnover varied from 0.00009 to 0.08 mg C/L/h, i.e., varying from negligible to a rate of 1.9 mg C/L/d. However, for May there was aphotic production of POC, as opposed to aphotic turnover, at a rate of 0.074 mg C/L/d. During the months June to November the E_{act} varied between 50 and 76 kJ/g C, such a low activation energy means that the Q_{10} of this reaction was only 1.02, and so at 283 K the rate of POC turnover peaked at 0.131 mg C/L/h. During the same months for the photic processes, the value of $K_{max} = 1$ (mg C/L/h/W/m²); however, at the range of PAR experienced by the samples even in the height of summer, the rates never approached this value. Therefore, it is the variation in α that is important, the rates of photic loss were between 0.00002 and 0.0282 mg C/L/h. However, in the experiments in May and February photoproduction was predicted at rates of 0.00056 and 0.0042 mg C/L/h. In the proposed scheme POC can turnover into CO₂ or DOC; in the first few months of experimentation (December–April), the greater proportion of the POC turned over was to become DOC ($\mu = 61$ to 95%, i.e., between 61 and 95% of the POC lost becomes DOC before itself being turned over). For the experiments later in the year (June to November), the minority of the POC becomes DOC, and even in one case, no DOC was predicted as being produced from the turnover of POC. For the case of May when net production of POC occurred then the term μ represents the proportion of the POC production that comes from DOC, in this case 85%. The change in the fate of POC could be due to changes in the source of the POC with wet winter months dominated by POC eroded from the peat profile exposed in river banks or coming from overland flow. Later in the year, the POC may come from relatively fresh organic matter from vegetation.

For the phase that this study has labeled a priori as the labile DOC phase has rates of aphotic degradation that are very low with a maximum rate of 0.02 mg C/L/h, but as low as 0.000029 mg C/L/h, i.e., the aphotic rate of loss could be negligible (Table 2). This partly shows that the modeling scheme does not actually have to assume that one phase is always more labile than another or that one process is always faster than another. Further, a phase may appear labile to one process might be relatively refractory to another. The E_{act} varied from 0.9 to 40 kJ/g C similar to that for turnover of POC and is still remarkably low again suggesting that aphotic degradation of this labile DOC phase is insensitive to changes in stream temperature. With regard to the photic degradation of the labile DOC phase, the value of K_{max} does not vary much from 1 and with rate of

Table 2. The Summary of Model Parameters for the Turnover of DOC₁—The Most Labile DOC Fraction

Month	[DOC] ₀	[POC] ₀	A	E _{act}	K _{max}	α	Fraction (μ)
Dec	27	10	0.022	0.00009	3.00	0.00070	0.04
Feb	58.3	26	0.00019	0.01000	0.900	0.00080	0.07
Mar	29.9	9.5	0.005	0.03997	0.899	0.00103	0.93
April	57	25	0.00004	0.004	1.000	0.00008	0.03
May	28	24	0.00012	0.004	1.000	0.00093	0.19
June	33	23	0.0054	0.004	1.000	0.00008	0.10
July	50	14	0.00012	0.004	1.000	0.00025	0.15
Aug	47	105	0.00003	0.004	3.000	0.00080	0.49
Oct	33	37.5	0.00056	0.004	1.000	0.00078	0.44
Nov	57.3	26	0.00011	0.004	1.000	0.00014	0.42

Table 3. The Summary of Model Parameters for the Turnover of DOC₂—The Most Refractory DOC Fraction^a

Month	[DOC] ₀	[POC] ₀	A	E _{act}	K _{max}	α	MAPE
Dec	27	10	−0.03446	0.18688	1.06352	0.000	13.6
Feb	58.3	26	−0.41809	0.11168	1.69026	0.037	9.5
Mar	29.9	9.5	−0.36708	0.39683	0.38772	0.021	1.0
April	57	25	−0.40476	0.14950	1.91083	0.266	8.0
May	28	24	0.00005	0.14950	1	0.800	21.4
June	33	23	2.4	0.15341	0.69788	0.371	27.0
July	50	14	−1.1	0.15341	0.70788	0.341	27.0
Aug	47	105	−0.10068	0.17640	0.04439	0.241	5.0
Oct	33	37.5	−0.55515	0.39947	1.75602	0.247	4.4
Nov	57.3	26	0.017768	0.22980	0.00444	0.555	11.5

^aThe mean average percentage error (MAPE) for the fit of the entire model scheme.

photodegradation between 0.0001 and 0.001 mg C/L/h/W/m². In nine out of the 10 experiments the proportion of this DOC phase that transferred to the second DOC phase (μ —equation (3)) was in the minority except in the March experiment where 93% of the first phase transferred into the second phase.

The second DOC phase, the assumed refractory phase in the proposed scheme, had an aphotic degradation rate of up to 0.08 mg C/L/h with an E_{act} consistently higher than that of either the labile DOC or the POC with values ranging between 111 and 399 kJ/g C giving a Q_{10} of 1.08 at 283 K and showing that this phase would be more sensitive to changes in stream temperature than any other considered (Table 3). The apparent quantum yield of this phase is far higher than the other modeled phases with an α varying from 0.0004 to as high as 0.8 mg C/L/h/W/m².

It is difficult to compare results from this study with previously published results because of the detail of this study in allowing for POC and DOC turnover. Wickland *et al.* [2007] observed 6–15% conversion of pore water DOC to CO₂, and 10–90% conversion of the vegetation-derived DOC, during 1 month dark incubations, and del Giorgio and Pace [2008] measured rates of loss as low as 0.4%/d, but again for dark incubations of fluvial DOC. The latter study was also for samples from near the tidal limit of the Hudson River, i.e., samples that would already have been in the river for many days. Stutter *et al.* [2013] found losses of DOC as low as 5% over 41 days, but the experiments were performed on filtered DOC separated from its original solution, freeze-dried prior to experimentation, and on comparatively old DOC compared to this study. Dawson *et al.* [2001] did consider a short river reach (2 km) in a peat headwater and estimated that 12–18% of DOC was removed over such a short reach, i.e., rapid removal. Rates of photodegradation have been reported in lakes, e.g., Graneli *et al.* [1996] measured rates between 0.009 and 0.4 mg C/L/d. Most values of AQY in the literature are defined for single wavelengths [e.g., Boyle *et al.*, 2009] or for inappropriate end products making them less

transferrable to this study [e.g., Stubbins *et al.*, 2010]. Osburn *et al.* [2009] measured AQY for DOC values between 1 and 3 mmol C/mol photons, for samples at the mouth of the Mackenzie River (1,805,200 km²). It is difficult to find studies that measure activation energy in comparative systems, but Alperin *et al.* [1995] give a value of 6.7 kJ/g C for DOC in marine sediments; a higher value may be expected for DOC that is likely to have been older and more recalcitrant than that found in rivers. Soumis *et al.* [2007] give photoreactivity of DOC in sterile lake water as between 15.5 and 35.8 mg CO₂/kJ. This larger

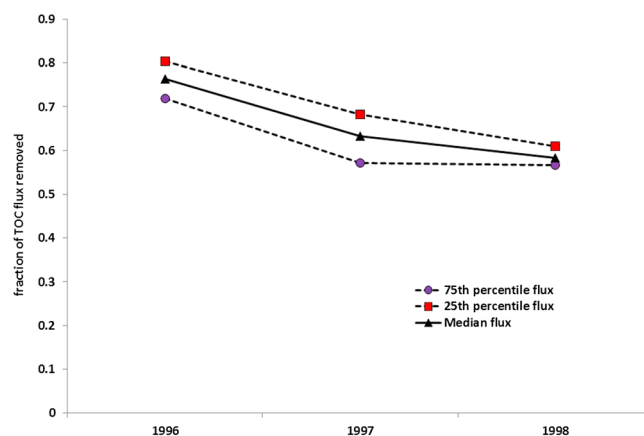


Figure 7. The fraction of total organic carbon (TOC) flux removed across the study catchment for 3 years (1996–1998) based upon the median, 25th and 75th percentile predicted input flux of DOC and POC.

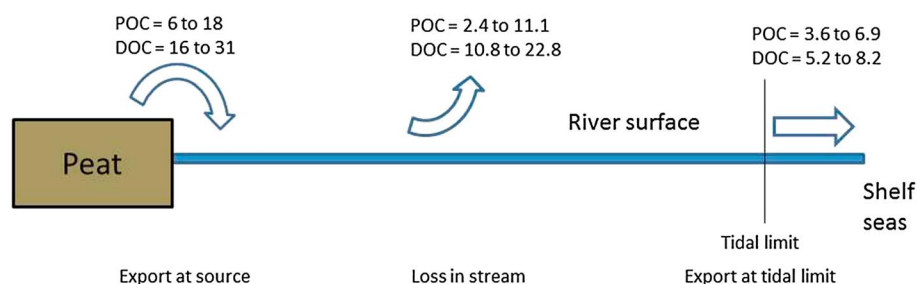


Figure 8. Schematic diagram of the exports and fate of organic matter transported into and out of the River Tees as predicted by this modeling scheme.

photoreactivity may be due to the experiment being performed in sterile containers that remove any biotic process and so photic processes are the only process operating.

3.1. Application

The best fit model derived from the observed hourly data for Cottage Hill Sike was

$$\ln(\text{DOC}) = 2.72 + 0.0099 \text{ year} - 0.432 \sin\left(\frac{\pi m}{6}\right) - 0.305 \cos\left(\frac{\pi m}{6}\right) - 0.073Q + 0.037 \ln Q \quad (14)$$

$$n = 935, r^2 = 0.92$$

where year = the year in the record since 1993. The quality and physical interpretation of this model is not the focus of this study, but it should be noted that there was a significant trend in DOC concentration over the period of record. It should also be noted that when considered on hourly flows, the concentration of DOC decreases with increasing discharge. The median DOC concentration over the years of interest was 19.8 mg C/L. The POC rating curve was already established (equation (11)) and for the years of interest the median POC concentration was 3.9 mg C/L. The estimated in-stream residence time for water between Trout Beck and the tidal limit (at Broken Scar—Figure 3) varied from 12.9 to 127.2 h with a median of 35 h.

The above approach predicts that the flux of POC at source was between 6 and 18 t C/km²/yr and for DOC was between 16 and 31 t C/km²/yr (Figures 7 and 8). The POC loss was between 2.4 and 11.1 t C/km²/yr and the DOC loss was between 10.8 and 22.8 t C/km²/yr. The POC loss rate was between 20 and 43%, and the DOC loss rate was between 63 and 75%. Given that the modeling includes the transformation of POC into DOC and vice versa, it is perhaps more appropriate to consider the export and loss of TOC (POC + DOC). The export of TOC from the source was calculated to be between 22 and 49 t C/km²/yr, with the loss between 13 and 33 t C/km²/yr giving a TOC loss rate of between 53 and 62%—very similar for both Sweden [Humborg *et al.*, 2010] or for the Yukon basin [Striegl *et al.*, 2012]. However, the overall export and loss of TOC belies the capacity of the catchment to process DOC since the transformation of POC into DOC has been included in the calculations. For the application of the model the average value of μ was 0.66, therefore, between 3.2 and 5.7 t C/km²/yr of POC would have been converted to DOC, and thus, the equivalent export of DOC was between 19.5 and 36.3 and loss was between 14.7 and 27.9 t C/km²/yr at a loss rate between 70 and 79%.

The predicted DOC loss rate is slightly larger than that predicted for this catchment by Moody *et al.* [2013] at between 48 and 69%. Moody *et al.* [2013] estimated an equivalent removal rate of DOC for this catchment of between 7.7 and 21.4 t C/km²/yr, and although particulates were included in the experiment, the loss rate of POC was not estimated nor was the diurnal cycle considered. It might be that because this study includes a diurnal cycle and that aphotic rates of degradation are so small that ignoring diurnal cycles would lead to an overestimation of DOC and POC turnover. However, it would seem that the previous approach of Moody *et al.* [2013] could not capture the very rapid initial decline of DOC in daylight.

4. Discussion

This study has proposed a mechanism for organic matter turnover in rivers, and the fit of the scheme, based on the assessing of the number of forms of POC and DOC as assessed by use of AIC on the scheme fits, has suggested that turnover can be accounted for by three phases: POC, labile DOC, and refractory DOC and that there is production of DOC and POC within stream water. Worrall *et al.* [2013] when considering the impact

of diurnal cycling upon flux calculations proposed a simple two rate model for DOC loss based on separate zero-order rates for day and night. This study would confirm that separate rate laws for day and night are appropriate but that a zeroth-order rate law for daylight conditions would be too slow and that second order would be better. A number of studies have proposed different types of DOC when considering DOC turnover; *Gregorich et al.* [2003] used a double exponential model to explain their degradation rates in the dark, and *Kalbitz et al.* [2003] describe their results in terms of labile and refractory DOC. It is possible that the model scheme proposed here should include a very refractory form of DOC so that predicted DOC concentration never declines to zero. In the scheme proposed above although the aphotic processes were allowed to vary with temperature, the photic processes only varied with light intensity; it may be more realistic that temperature also plays a role, and therefore, we should look for kinetic laws that contain an interaction term between PAR and T .

Several attempts have been made to quantify the loss of DOC across a catchment. *Worrall et al.* [2006] used a mass balance approach to calculate the DOC export at a range of scales to show an average net loss of 40% of DOC from source to outlet across the same catchment as studied here. *Worrall et al.* [2007] used nationally collected monitoring data for biochemical oxygen demand (BOD) as a measure of DOC turnover and found an average 31% loss across the UK fluvial network—equivalent to an additional release of 1 t C/km²/yr across the entire UK land surface. However, in basing their approach upon BOD data a fixed fluvial residence time of 5 days was assumed—a long residence time for the short, relatively unimpounded rivers of the UK. What is more, BOD tends to be measured further downstream in the fluvial network and away from sources of fresh more readily degraded DOC. Alternatively, *Worrall et al.* [2012] used empirical and structural modeling of the DOC export from over 194 catchments across the UK, across 7 years and in comparison to the soil, land use, and hydroclimatic characteristics of each catchment to assess net watershed losses. A net watershed loss of DOC up to 78% was found, equivalent to between 9.0 and 12.7 t C/km² of UK land area/yr. The measurement of DOC loss by mass balance studies might be thought of as not being affected in the same way by diurnal cycles as estimates based upon degradation experiments that were based upon daily sampling. However, mass balance studies have the same issue of bias that daily experiments do. Mass balance studies are based upon flux calculations, and except for a very few cases, flux calculations from catchments are based upon samples taken during daylight hours and not samples distributed across the diurnal cycle. *Worrall et al.* [2013] showed that not accounting for the diurnal cycle in this study catchment overestimated the DOC flux by 6%.

But the above does not consider the turnover and flux of POC. *Worrall et al.* [2007] used particulate fluxes published by the OSPAR Commission [OSPAR Commission, 2007] to give a value for the POC flux of 554 Mt/yr for the UK (equivalent to 2.3 t C/km²/yr). There are several problems with this approach, but of greatest relevance to this study is that the data were for suspended solids and not for particulate organic carbon, and the composition of the suspended sediment had to be assumed from published studies from across the UK [e.g., *Hillier*, 2001]. Given that the flux estimate of *Worrall et al.* [2007] was for tidal limit, and the turnover rate estimated from this study was between 20 and 43% so suggesting that the POC flux at soil source was between 693 and 972 kt C/yr (equivalent to 2.8 and 4 t C/km²/yr for the area of the UK) which would mean that turnover of POC from UK rivers would contribute between 139 and 418 k C/yr to the atmosphere—equivalent to between 0.6 and 1.7 t C/km²/yr for UK land surface.

Peatlands are known to be significant sources of DOC and POC, and although these components are commonly included in carbon budgets for these environments [e.g., *Billett et al.*, 2004; *Roulet et al.*, 2007], the turnover of these components into the atmosphere is not. However, when considering the greenhouse gas budget of peatlands, or indeed any other ecosystem, it is not the loss of DOC or POC that is as important as the turnover of the fluvial organic matter components. *Worrall et al.* [2011] assumed a 40% loss rate for DOC when calculating the greenhouse gas budget for a peatland and for the benefit of revegetation, but could not include a loss rate for POC even though it was the flux of POC that showed the greatest decrease of any flux upon revegetation. The POC flux from bare peat was as high as 206 t C/km²/yr, while the POC flux for revegetated plots was as low as 6 t C/km²/yr. Given the median loss rate for POC found in this study, then the GHG impact of POC loss from eroding peatlands would be 77 t C/km²/yr or 282 t CO_{2eq}/km²/yr compared to 2.4 t C/km²/yr (8.7 t CO_{2eq}/km²/yr) for revegetated peat plots. Therefore, a consideration of DOC and POC turnover from eroding systems shows the benefit of revegetation has been underestimated.

Further still, this calculation of the GHG impact is based on the assumption that all loss is as CO₂ and not as the powerful greenhouse gas CH₄. *Striegl et al.* [2012] noted the 6.4% of the greenhouse gas warming potential of the emissions from the Yukon were due to CH₄.

There are limitations to the approach suggested here. The model scheme would predict that at some time the value of DOC concentration could decline to zero, but this was never observed over the 10 sets of experiments over 70 h in this study nor was it observed over periods 10 days in the experiments of *Moody et al.* [2013]. Therefore, this scheme may struggle to predict the long-term DOC concentration; however, residence times of greater than 70 h were rarely observed for the UK context. It is also not clear from this work what controls the range of input parameters, and this study had to resort to randomly selecting between the sets of input parameters from the 10 monthly experiments. Although it is possible to constrain the parameter space from these experiments, we cannot comment on which parameter set should be used at any given time.

The other major limitation of this study is in attempting to measure in situ degradation of fluvial organic carbon to provide data to model. This study used multiple quartz tubes to measure degradation (and production) over 70 h in each of 10 months. The relative small size of the quartz tubes created three problems. First, the quartz tubes were not the depth of the river over all flow conditions considered and so the full range of light attenuation in the study stream could not be measured by this approach. In the worst case the methodology represented only 25% of the light conditions in the source stream, but at the same time it represented 46.5% of the flow depths. Given the transit time of the study stream, most of the waters in the stream would be expected to have passed the tidal limit within the time span considered by the experiments, and over such a time span the light penetration would have increased and light attenuation lessened. Second, the small tubes could not be stirred and so although suspended sediment was not excluded from these experiments as is common in DOC degradation experiments [e.g., *Stutter et al.*, 2013]. However, it is clear that the experimental approach was able to record POC production and degradation, but without stirring, the contribution of POC to light attenuation would have been limited. Third, the small quartz tubes could have acted to heat the sampled stream water above the ambient air temperature. The tubes were loosely stoppered to allow air transfer and ambient conditions were monitored but the temperature in the tubes was not logged.

The small size of the tubes did mean that it was easier to run more samples within each months experiment, whereas it may have been difficult to run multiple mesocosms over the same period. The small tubes meant that very fresh samples from the DOC source could be studied at very short time scales (within an hour of sampling). All the tubes could run under ambient conditions which facilitated comparison with natural conditions, and the whole stream samples were used without separating out POC and DOC.

5. Conclusions

This study has shown that the subdaily turnover of organic matter in streams could be represented by photic and aphotic processes, both degradation and production, acting on three phases (POC, labile DOC, and refractory DOC). The turnover mechanisms and scheme were found to fit well to 10 months of experiments with a MAPE of 13%. The mechanisms suggested that processes in the dark were slow to negligible but that DOC could accumulate overnight due to faster turnover of POC. The study suggests turnover rates of between 20 and 43% for POC, 63 and 75% for DOC, and 53 and 62% for TOC across a river system with a residence time between 12 and 127 h.

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